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SYNTHESIS OF 2,3-DIMETHYLTETRACYCLO(5.5.1.$0^{4,13}$.$0^{10,13}$)TRIDECA-2,5-DIEN-9-ONE, A NEW DERIVATIVE OF ALL-*CIS*-(5.5.5.5)FENESTRANE

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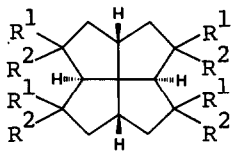
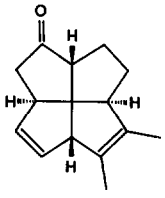
Abstract—Intramolecular arene–olefin photoreaction of methyl-6-methyl-2-phenylhept-5-enoate (**9a**) leads to the tetracyclic product **10a**, from which the fenestra-dienone, **2**, has been obtained. Mechanistic aspects of the photoreaction are discussed.

Fenestranes are unique amongst strained hydrocarbons because of the planoid deformations around the central carbon atom.[1] Not only for this reason but also for the purely synthetic challenge these structures with a central atom, which is common to four rings, have found increasing attention.[2] For all-*cis*-(5.5.5.5)fenestrane (**1a**) and the tetraketone, **1b**,



1a $R^1=R^2=H$
b $R^1+R^2=O$



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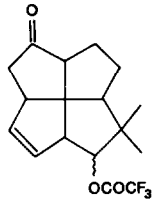

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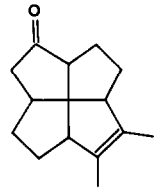

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syntheses have been reported based either on the symmetry of intermediates and on the target molecule[2a,d] or on the symmetry of the parent compound[2b,c,e,f] and make use of the "common atom approach".[3] It now has been found that an "unsymmetrical" synthetic pathway leading to an unsymmetrically substituted (5.5.5.5)fenestrane provides a short, efficient synthesis of **2**, a functionalized all-*cis*-(5.5.5.5)fenestrane. This reaction sequence is based upon an intramolecular arene–olefin cycloaddition,[4] which at present is one of the most attractive transformations by which dearomatization[5,6] of a phenyl ring with concomitant formation of several C—C bonds can be achieved.

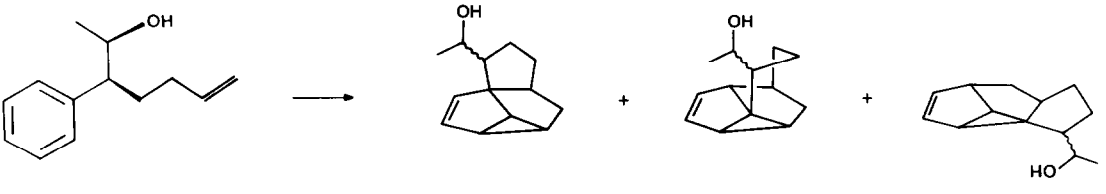
Four structurally different types of tetracyclic products have so far been detected in the intramolecular photoaddition of substituted 5-phenylpentenes.[7]

Three of them have been found in the photoreaction of (*RS*/*SR*)-3-phenylhept-6-en-2-ol. Compound **5** gave the tetracycloundecanes, **6** and **7**, both of which are formed as pairs of configurational isomers and the "linear" tetracyclic compound **8** as a single isomer.†[8]

Photolysis of **9a** in degassed hexane gave a mixture of three products from which the major two components could be isolated in pure form by preparative HPLC separation. Structure elucidation revealed the formation of two types of unsaturated tetracycloundecanes in high configurational purity (Scheme 2). Taking the structures found earlier in photoreactions of 5-phenylpentenes into consideration,[4,9,10] the structure of **10a** and **11a** could be established by NMR spectroscopy.

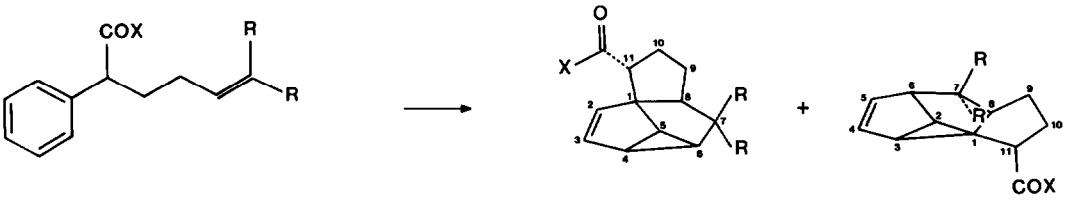
Apart from the olefinic C atoms, the ^{13}C-NMR spectrum of **10a** shows five doublets, one of which could clearly be assigned to C-11. The three C atoms, which form the cyclopropyl ring are apparent from delay-time experiments. The ^{1}H-NMR spectrum of **10a** revealed a coupling pattern indicative of a substituted vinylcyclopropane structure. INDOR experiments showed that H-5 is coupled to two protons, only one of which is coupled to an adjacent olefinic proton. Since the two protons, coupled to H-5 do not exhibit the AB

† All compounds discussed are racemic mixtures.



5 **6** **7** **8**

Scheme 1.



	R	X
9a	CH_3	OCH_3
b	H	OCH_2CH_3

	R	X
10a	CH_3	OCH_3
b	H	OCH_2CH_3
12	CH_3	OH
13	CH_3	$OCOOCH_2CH(CH_3)_2$
14	CH_3	CHN_2

	R	X
11a	CH_3	OCH_3
b	H	OCH_2CH_3

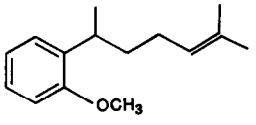
Scheme 2.

coupling pattern of a CH_2 group, the connectivity of the vinylcyclopropane substructure in **10a** can be established.

Exo-configuration was assigned to the carbomethoxy substituent by Eu-shift experiments, which gave a significant change for the proton at H-2. For **11a** the ^{13}C-NMR spectrum and delay-time experiments indicated the presence of a three-membered ring, with only two protons attached to it. The ^{1}H-NMR spectrum of **11a** revealed the presence of one proton each at both allylic C atoms. The presence of the cyclopentene substructure in **11a** was demonstrated by INDOR experiments, which indicated that both these allylic protons are coupled to the same proton. The configuration of the carbomethoxy group in **11a** has not yet been established. At present, we favour the *exo*-configuration because **11a** should have been formed from the same conformation as **10a** (see below). This configuration is further supported by the observation that the product **11b**, obtained in the photolysis of ethyl-2-phenylpent-5-enoate (**9b**) could be photoisomerized to **10b** (J. Mani and R. Keese, unpublished).

From mechanistic and product studies it has been concluded that *meta*-photoaddition of an olefin to benzene takes place if both chromophores have similar or identical ionization potentials.[11]

The selectivity in this photoreaction is strongly controlled by its substituents. For example, in the intramolecular photoreaction of 5-phenylpentenes, a methoxy or methyl group in the *ortho*-position of the phenyl ring leads preferentially to a 1,3-addition. Thus,



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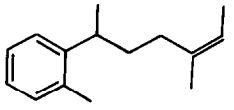

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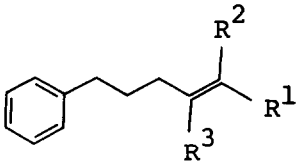
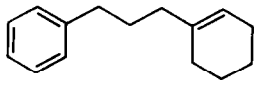


	R^1	R^2	R^3
17	H	H	H
18	CH_3	H	H
19	H	CH_3	H
21	CH_3	CH_3	CH_3



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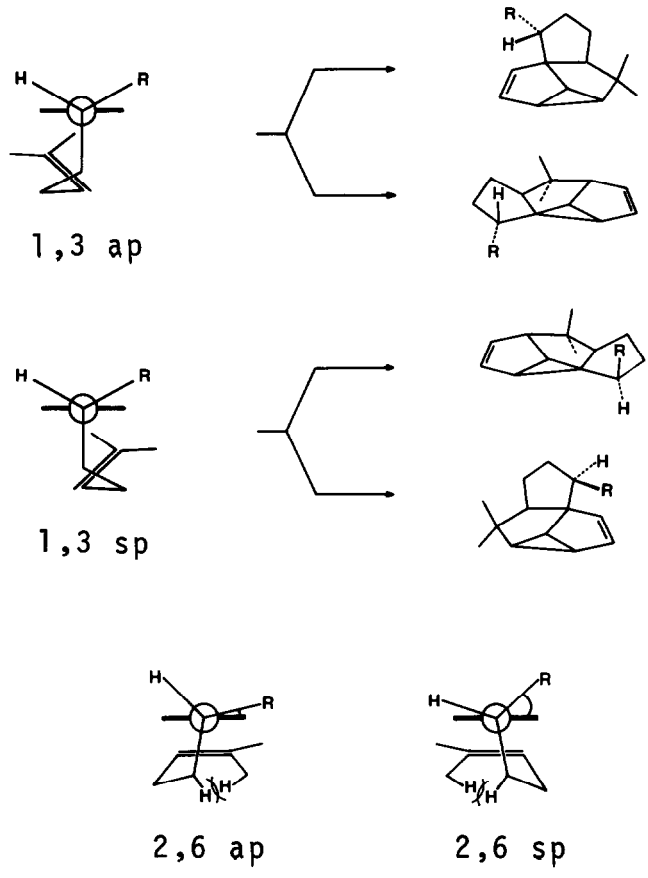

Scheme 3.

the formation of photoproducts from **15** and **16** could be explained by the stabilizing effect of these electron donor substituents which is exerted during the formation of the primary photoadduct.[9] In the absence of substituents in the phenyl ring, the 5-phenylpentenes **17**, **18** and **20** show a greater tendency for 2,6-addition,[10] indicating that the stabilizing effect during the formation of the primary photoadduct can also be exerted by the electron donor properties of the aliphatic side chain itself. However, Morrison has already observed that *cis*-6-phenylhex-2-ene (**19**) leads preferentially to products which are derived from 1,3-addition.[4] Similarly, 2,3-dimethyl-6-phenylhex-2-ene (**21**) gave products derived from 1,3-addition.[9] In the case of methyl-6-methyl-2-phenylhept-5-enoate (**9a**), the two major products which have been isolated are also formed via 1,3-addition. Apparently a *Z*-substituent at the terminal C atom of the double bond reduces 2,6- and enhances 1,3-addition. This remarkable difference between *Z*- and *E*-6-phenylhexene and their derivatives in *meta*-photoaddition may be analysed in terms of conformational preferences.[7]

In 5-substituted 5-phenylpentenes, e.g. **9a**, **17**, **19**, **20**† or **21** the intramolecular *meta*-photoreaction can occur via 1,3- or 2,6-addition of the double bond to the arene. The 1,3- and the 2,6-reaction each could arise from two different conformations. The allylic group is defined either as *anti*-planar or *syn*-planar with respect to a particular substituent in the benzylic position (Scheme 3). Since steric repulsions between a particular *Z*-substituent at the terminal end and the protons in the 4-position of 5-phenylpentene in both the *syn*- and the *anti*-planar conformation favouring a 2,6-attack, the 1,3-addition should be preferred. This tendency is enhanced by donor substituents in the *ortho*-position of the phenyl ring.[8,9]

In accordance with this analysis, **10a** and **11a** are formed via the 1,3-mode. The configuration of the carbomethoxy group in **10a** and **11a** may be due to differences in interactions between the benzylic substituent R and the phenyl ring. Model considerations suggest that the 1,3-*syn*-planar conformation is less stable than the 1,3-*anti*-planar arrangement. The tetracyclic ester **10a** was readily transformed into the all-*cis*-(5.5.5.5)fenestradienone, **2**. Treatment of the mixed anhydride **13**, obtained from the acid **12** with diazomethane, gave the diazoketone **14**.[12] Reaction of this compound with CF_3COOH gave the fenestranes **2** and **3** in a ratio of 2.2 : 1. The structures of **2** and **3** were established by ^1H- and ^{13}C-NMR spectroscopy.‡ The ^{13}C-NMR spectrum of **2** reveals the presence of two double bonds. The fact that two of these ^{13}C signals appear as singlets is proof of the migration of one of the methyl groups during the ring closure reaction of **14**. The 400 MHz ^1H-NMR spectrum of **2** shows separate signals for the protons at C-1–C-10 (Fig. 1).

† Photoreactions of substituted 5-phenylpentenes, in which the double bond forms part of a ring, lead to a variety of products, not readily reconcilable with conformational preferences.[10]

‡ Configuration of the protons at C-8 are specified relative to H-7; correspondingly, protons at C-11 and C-12 are specified relative to H-10.[13]

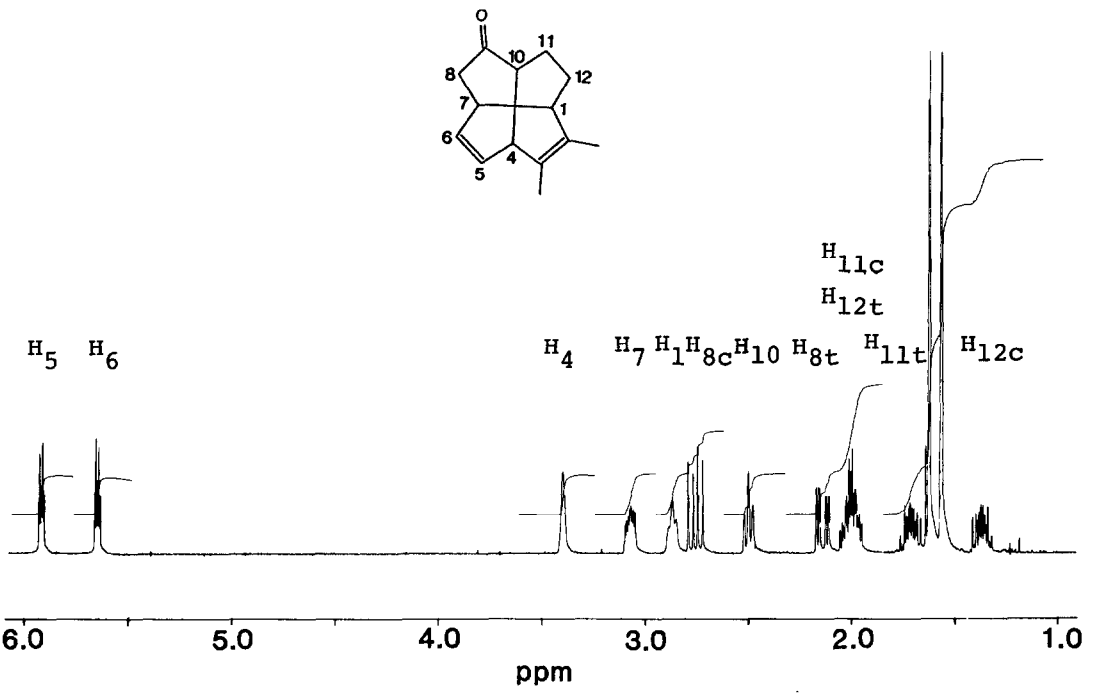

Fig. 1.

The coupling pattern of the olefinic protons showed interaction with the two allylic protons at C-4 and C-7. The proton at C-7 is further coupled to the two protons at C-8 ($J_{H\text{-}7\text{–}H_{cis}\text{-}8}$ = 10.3 Hz, $J_{H\text{-}7\text{–}H_{trans}\text{-}8}$ = 5.9 Hz). The *trans* proton at C-8 shows *W* coupling to H-10 (J = 1.6 Hz). Final proof for the all-*cis* configuration of **2** comes from NOE experiments, which reveal a *cis* relationship for H-4–H-10 as well as for H-1–H-7. Since a *trans* relationship had been established for H-7–H-10 and no NOE was found for H-7 or H-1 when H-4 was irradiated, we conclude that **2** has the all-*cis* structure shown.

Based upon MNDO calculations for all-*cis*-(5.5.5.5)fenestrane (**1a**) and similar structures[1b,e] (W. Leuf and R. Keese, unpublished) as well as the X-ray structure analysis of **1b**,[14] we may conclude that the central C atom of **2** has two bond angles, which are close to 115°. By hydrogenation of one of the double bonds, the fenestradienone **2**, being sensitive to oxygen, is transformed into **4**.

A new derivative of all-*cis*-(5.5.5.5)fenestrane (**1a**) has been prepared from methylphenylacetate in six steps with an overall yield of 2.3%. The functionalities in three of the four rings will lead to the preparation of further unsaturated derivatives of (5.5.5.5)-fenestrane.[1,15]

EXPERIMENTAL†

Methyl-6-methyl-2-phenylhept-5-enoate (**9a**). To a soln of 11.3 g (0.11 mol) di-isopropylamine in 70 ml THF was added 73 ml of *n*-BuLi (1.3 mol) in hexane at −70°. After stirring for 1 hr at 0°, the soln was cooled again and 14.0 g (93 mmol) methylphenylacetate and, subsequently, 19.6 g (93.3 mmol) 5-iodo-2-methylpent-2-ene[17] in 100 ml THF were added slowly. The mixture was stirred at 0° for 14 hr, worked-up and twice distilled in a kugelrohr (b.p. 110–120° at 0.1 Torr). An analytically pure sample of **9a** was obtained by flash chromatography[18] with hexane–*t*-butylmethylether (20:1). Compound **9a** was unstable at 20°. R_f (*t*-butylmethylether–ether, 7:4) 0.60; b.p. 105° (0.2 Torr). IR ν_{max} cm^{-1}: 3100–2850, 1730, 1490, 1450, 1430. ^{1}H-NMR: δ 1.5 (s, 3H), 1.63 (s, 3H), 1.8–2.2 (stack, 4H), 3.4–3.6 (stack, 4H), 4.9–5.2 (m, 1H), 7.2 (s, 5H). MS: *m/z* 232 [M]$^+$, 150, 173, 118, 104, 91, 83, 69, 55, 41. UV λ_{max} nm: 263 (2.26), 257 (2.37), 251 (2.30). (Found: C, 77.61; H, 8.78. Calc for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.)

Photoreaction of **9a**. A degassed soln of 6.35 g (27.3 mmol) **9a** in 350 ml hexane was irradiated with a 500 W Hanovia lamp for 25 hr. The mixture was concentrated and purified by flash chromatography with hexane–*t*-butylmethylether (7:4). Subsequent preparative HPLC with hexane–*t*-butylmethylether (100:1) gave 0.727 g (3.2 mmol, 12%) of **10a** and 0.960 g (4.2 mmol, 16%) of **11a** as colourless oils.

Compound **10a**. R_f (hexane–*t*-butylmethylether, 7:4) 0.59. IR ν_{max} cm^{-1}: 2955, 1730, 1435, 1360, 1168. ^{1}H-NMR: δ 1.05 (s, 3H), 1.14 (s, 3H), 1.4–2.2 (stack, 7H), 2.47 (t, J = 6.4 Hz, 1H), 2.85 (t, J = 8 Hz, 1H), 3.63 (s, 3H), 5.21 (d, J = 5.8 Hz, 1H), 5.65 (dd, J = 5.8, 2 Hz, 1H). ^{13}C-NMR: δ 28.9 (q), 29.04 (q + t), 30.8 (t), 32.1 (d), 41.5 (s), 43.6 (d), 45.2 (d), 50.9 (q), 51.3 (d), 70.2 (d), 70.4 (s), 129.0 (d), 134.3 (d), 174.6 (s). MS: *m/z* 232 [M]$^+$, 173, 157, 150, 145, 131, 117, 107, 105, 91, 77. (Found: C, 77.16; H, 8.83. Calc for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.)

Compound **11a**. R_f (hexane–*t*-butylmethylether, 7:4) 0.58. IR ν_{max} cm^{-1}: 2950, 1730, 1435. ^{1}H-NMR: δ 0.80 (s, 3H), 1.02 (s, 3H), 1.3–2.25 (stack, 6H), 2.38 (t, J = 6 Hz, 1H), 2.52 (m, 1H), 2.7 (dd, J = 6, 2.1 Hz, 1H), 3.63 (s, 3H), 5.45 (dd, J = 2.1, 5.5 Hz, 1H), 5.67 (dd, J = 5.5, 2.2 Hz, 1H). ^{13}C-NMR: δ 23.02 (q), 23.95 (t), 24.13 (q), 31.71 (t), 34.62 (d), 43.16 (d), 47.95 (s), 48.21 (d), 48.8 (d), 50.87 (q), 57.0 (s), 62.99 (d), 129.35 (d), 131.5 (d), 174.9 (s). MS: *m/z* 232 [M]$^+$, 173, 167, 157, 145, 131, 115, 107, 91, 77. (Found: C, 77.60; H, 8.79. Calc for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.)

7,7 - *Dimethyl* - 11 - *carbohydroxy* - *tetracyclo* - (6.3.0.0^{1,5}.0^{4,6})*undec* - 2 - *ene* (**12**). A soln of 0.159 g (0.684 mmol) **10a** and 1.37 mmol KOH aq in 5 ml MeOH was refluxed for 2.5 hr. After work-up, the crude acid, crystallizing on standing, was chromatographed with hexane–EtOAc (3:1) to give 0.142 g (0.65 mmol, 95%) of **12**. A pure sample was

† For general remarks see Mani *et al.*[8] and Schori *et al.*[16]

obtained by recrystallization from pet-ether–Et_2O, m.p. 105–106°; R_f (hexane–EtOAc–HOAcOH, 50:16.7:1) 0.38. IR ν_{max} cm^{-1}: 3010, 2960, 2870, 1709. ^{1}H-NMR: δ 0.9–2.2 [stack with 1.0 (s) and 1.08 (s), 13H], 2.43 (t, J = 6.4 Hz, 1H), 2.82 (t, J = 8 Hz, 1H), 5.30 (d, J = 5.8 Hz, 1H), 5.62 (dd, J = 5.8, 2 Hz, 1H), 10.6 (br, 1H). MS: *m/z* 219 $[M]^+$, 173, 162, 157, 150, 145, 136, 131, 117, 105, 95, 91, 83. (Found: C, 76.75; H, 8.36. Calc for $C_{14}H_{12}O_2$: C, 77.03; H, 8.31%.)

7,7 - *Dimethyl* - 11 - *diazoacetyl* - *tetracyclo* - (6.3.0.0^{1,5}.0^{4,6})*undec*-2-*ene* (**14**).[12] A soln of 0.208 g (0.95 mmol) acid **12** in 3 ml Et_2O was treated with 133.3 μl (0.96 mmol) Et_3N and 124 μl (0.96 mmol) *s*-butylchloroformiate at −15°. After addition of more Et_2O, the mixture was filtered through a sintered frit[19] and ethereal diazomethane (~1.6 mmol) added at −15°. After stirring for 15 hr at 0°, $NaHCO_3$ aq was added. After drying over $NaSO_4$ the solvent was removed at 10–20° and the yellow residue gave, after chromatography[20] with hexane–*t*-butylmethylether (7:4) 0.1 g (0.41 mmol, 43%) of **14** as a yellow oil. R_f (hexane–*t*-butylmethylether, 7:4) 0.37. IR ν_{max} cm^{-1}: 3030, 2100, 1638, 1369, 1320. ^{1}H-NMR: δ 1.05 (s, 3H), 1.12 (s, 3H), 1.32–2.15 (stack, 7H), 2.42 (t, J = 6.4 Hz, 1H), 2.82 (t, J = 8 Hz, 1H), 5.15 (s, 1H), 5.27 (d, J = 5 Hz, 1H), 5.76 (dd, J = 5, 2 Hz, 1H). MS: *m/z* 242 $[M]^+$, 214, 202, 199, 163, 145, 143, 129, 128, 117, 116, 115, 91, 77, 75, 73.

2,3 - *Dimethyltetracyclo*(5.5.1.0^{4,13}.0^{10,13})*tridec* - 2,5 - *dien* - 9 - *one* (**2**). A soln of 45.6 mg (0.19 mmol) **14** in 0.3 ml CH_2Cl_2 was added to 1.5 ml trifluoroacetic acid at 0°. After evolution of N_2, H_2O was added and the mixture worked-up. The yellow oil was chromatographed[20] with hexane–*t*-butylmethylether (7:4) and yielded 22 mg (0.103 mmol, 54%) of **2**, in a purity of 89%, as a colourless oil. A pure sample of air-sensitive **2** was obtained as an oil by repeated chromatography. R_f (hexane–*t*-butylmethylether, 7:4) 0.52. IR ν_{max} cm^{-1}: 3050, 3010, 2960, 2930, 2910, 2860, 1730, 1448. ^{1}H-NMR: δ 1.38 (H_{cis}-12), 1.57 (3H), 1.63 (3H), 1.71 (H_{trans}-11), 1.94–2.06 (H_{cis}-11 and H_{trans}-12), 2.15 (H_{trans}-8), $J_{H_{trans}\text{-}8\text{–}H_{cis}\text{-}8}$ = 18.5 Hz, $J_{H_{trans}\text{-}8\text{–}H\text{-}7}$ = 10.6 Hz, $J_{H_{trans}\text{-}8\text{–}H\text{-}10}$ = 1.6 Hz, 2.5 (H-10), $J_{H\text{-}10\text{–}H_{cis}\text{-}11}$ = $J_{H\text{-}10\text{–}H_{trans}\text{-}11}$ = 8.1 Hz, 2.76 (H_{cis}-8), $J_{H_{cis}\text{-}8\text{–}H_{trans}\text{-}8}$ = 18.5 Hz, $J_{H_{cis}\text{-}8\text{–}H\text{-}7}$ = 10.3 Hz, 2.88 (H-1), $J_{H\text{-}1\text{–}H_{cis}\text{-}12}$ = $J_{H\text{-}1\text{–}H_{trans}\text{-}12}$ ≈ 7.5 Hz, 3.07 (H-7), $J_{H\text{-}7\text{–}H\text{-}6}$ = $J_{H\text{-}7\text{–}H\text{-}5}$ = 2.19 Hz, 3.41 (H-4), $J_{H\text{-}4\text{–}H\text{-}5}$ = $J_{H\text{-}4\text{–}H\text{-}6}$ = 2.19 Hz, 5.64 (H-6), $J_{H\text{-}6\text{–}H\text{-}5}$ = 5.60 Hz), 5.91 (H-5). ^{13}C-NMR: δ 12.6 (q), 12.9 (q), 31.0 (t), 32.8 (t), 43.2 (t), 51.6 (d), 60.5 (d), 64.9 (d), 65.2 (s), 69.4 (d), 131.5 (s), 132.5 (d+s), 133.0 (d), 220.3 (s). MS: *m/z* 214 $[M]^+$, 199, 172, 171, 157, 143, 129, 128, 117, 115, 91, 77. High resolution MS: found 214.1385; calc for $C_{15}H_{18}O$ 214.1383.

2,2 - *Dimethyl* - 3 - *trifluoracetoxy* - *tetracyclo* - (5.5.1.0^{4,13})*tridec* - 5 - *en* - 9 - *one* (**3**). R_f (hexane–*t*-butylmethylether, 2:1) 0.6. IR ν_{max} cm^{-1}: 3055, 3038, 2960, 2940, 2917, 2878, 2860, 1795, 1730, 1450, 1379. ^{1}H-NMR: δ 0.89–1.40 (stack, 2H), 1.40–1.95 (stack, 8H), 2.08–2.40 (stack, 2H), 2.52–2.83 (stack, 2H), 3.0–3.52 (stack, 2H), 4.73 (s, 1H), 5.50 (m, 1H), 5.70 (m, 1H). MS: *m/z* 328 $[M]^+$, 214, 146, 145, 132, 131, 117, 115, 91, 69.

2,3 - *Dimethyltetracyclo*(5.5.1.0^{4,13}.0^{10,13})*tridec* - 2 - *en* - 9 - *one* (**4**). A soln of crude **2**, prepared from 0.093 mg (0.38 mmol) **14**, in 7 ml MeOH was hydrogenated with Pd–C (10%). The product was chromatographed[20] with hexane–*t*-butylmethylether (5:2) and gave 0.06 g (72%) of **4** as a colourless oil. An analytically pure sample was obtained by further HPLC and GLC purification. R_f (hexane–*t*-butylmethylether, 2:1) 0.49. IR ν_{max} cm^{-1}: 2950, 2930, 2860, 1729, 1458, 1445. ^{1}H-NMR: δ 0.82–1.0 (stack, 1H), 1.15–2.50 (stack, 17H), 2.60–2.90 (stack, 2H). ^{13}C-NMR: δ 12.6 (q), 12.7 (q), 29.4 (t), 31.4 (t), 31.6 (t), 34.3 (t), 44.3 (t), 45.7 (d), 60.4 (d), 62.8 (d), 63.4 (d), 67.2 (s), 131.7 (s), 132.7 (s), 222.3 (s). MS: *m/z* 216 $[M]^+$, 201, 188, 173, 160, 145, 134, 133, 132, 91, 73, 61, 45, 43. (Found: C, 83.14; H, 9.34. Calc for $C_{15}H_{20}O$: C, 83.28; H, 9.32%.)

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